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A PROCESS AND AN APPARATUS FOR PRODUCING CALCIUM CARBONATE VIA AN ENZYMATIC PATHWAY

FIELD OF THE INVENTION

The present invention generally relates to the field of calcium carbonate production obtained by precipitation. More particularly, it concerns a process for preparing precipitated calcium carbonate (hereinafter referred to as PCC) involving the use of an enzyme that directly supplies a source of bicarbonate ions which are required by the PCC production process. The present invention is particularly useful in the pulp and paper industry.

BACKGROUND OF THE INVENTION

Production of $CaCO_3$

Calcium carbonate is used in different fields, most importantly in the pulp and paper industry, where it is largely used for coating the paper after it has been pressed, thereby increasing the printing quality of the paper, as well as its color, smoothness, and strength.

The traditional process of forming solid $CaCO_3$ consists in bubbling carbon dioxide in milk of lime ($Ca(OH)_2$). This process allows a sufficient amount of CO_2 to solubilize and produce solid calcium carbonate according to the following equation:

$$Ca(OH)_2 + CO_2 \longleftrightarrow CaCO_3 + H_2O \qquad [1]$$

Reaction (1) is the result of the following reactions:

$$CO_2 + H_20 \longleftrightarrow H^+ + HCO_3^- \qquad [1a]$$

$$HCO_3^- \longleftrightarrow H^+ + CO_3^{-2} \qquad [1b]$$

$$Ca\,(OH)_2 \longleftrightarrow Ca^{2+} + 2\,OH^- \qquad [1c]$$

$$Ca^{2+} + CO_3^{-2} \longleftrightarrow CaCO_3 \qquad [1d]$$

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$$2\,OH^- + 2\,H^+ \longleftrightarrow 2\,H_2O \qquad [1e]$$

This reaction (1) is a rather slow reaction and one drawback thus encountered with the same is its low production yield as compared to the need of $CaCO_3$ in the pulp and paper industry or in other fields.

There is thus presently a need for a process for the production of $CaCO_3$ that provides a better production yield.

Conversion of CO_2 into hydrogen ions and bicarbonate ions

EP0991462; AU7753398; WO9855210; CA2291785 in the name of the Applicant disclose the use of the enzyme carbonic anhydrase to catalyse the hydration of CO_2 into hydrogen ions and bicarbonate ions. The reaction that allows for the production of bicarbonate in the presence of the enzyme is represented by equation [2]:

$$CO_2 + H_2O \xleftrightarrow{\text{enzyme}} H^+ + HCO_3^- \qquad [2]$$

The hydration kinetics of CO_2, with or without enzyme, has been the object of several scientific works. The reaction rate constant of non-catalysed (without enzyme) reactions is in the order of $0{,}035 s^{-1}$ (25°C, pH=7)[1]. At an elevated pH (pH > 10), the hydroxyl ions (OH^-) contribute to the catalysis, and consequently, the reaction rate constant can attain $8.5 \times 10^3\ s^{-1}$ at 25°C[2]. The catalysed reaction (with enzyme), can also be associated with an elevated reaction rate constant in the order of $1{,}4 \times 10^6$ (25°C, pH= 8.8)[3]. The ratio of the two reaction rate constants allows one to predict the CO_2 hydration kinetics, which can be in the order of 50 million times more elevated when an enzyme is present and depending on the experimental conditions.

WO9855210 in the name of the Applicant also discloses the possibility to recycle the liquid phase used for CO_2 absorption given bicarbonate ions and protons are removed by an auxiliary unit.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a process and an apparatus for the production of $CaCO_3$ that satisfies the above-mentioned need for a process that provides an increased production yield of precipitated calcium carbonate (PCC).

In accordance with the present invention, that object is achieved with a process for producing $CaCO_3$, charaterized in that it comprises the steps of:

a) catalysing the hydration of CO_2 contained in a CO_2-containing gas by means of an enzyme capable of catalysing the hydration of dissolved CO_2 into hydrogen ions and bicarbonate ions, thereby producing a solution containing bicarbonate ions and hydrogen ions, said enzyme being carbonic anhydrase;

b) reacting the bicarbonate ions contained in the solution obtained in step a) with calcium ions, thereby producing a solution containing $CaCO_3$;

c) precipitating the $CaCO_3$ contained in the solution obtained in step b); and

wherein the step b) comprises the step of:

– mixing the solution obtained in step a) with $Ca(OH)_2$, thereby providing simultaneously said calcium ions for $CaCO_3$ production and OH^- ions for H^+ neutralisation.

The $CaCO_3$ is thus produced from milk of lime ($Ca(OH)_2$) and CO_2 as in the prior art, although it shows an improved yield, as explained hereinafter.

As mentioned above, the traditional process of forming $CaCO_3$ consists in bubbling carbon dioxide in milk of lime ($Ca(OH)_2$). This process produces solid calcium carbonate according to the following equation:

$$Ca(OH)_2 + CO_2 \longleftrightarrow CaCO_3 + H_2O \qquad [1]$$

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This non catalyzed solubilization of gaseous CO_2 in an aqueous medium implies the following series of natural reversible reactions. The equilibrium constants of these natural reactions are well known in the prior art.

$$CO_2 + H_2O <\!\!-\!\!> H_2CO_3 \quad K \cong 600 \text{ à } 25°C \quad (K \cong [CO_2]/[H_2CO_3]) \quad [3]$$

$$H_2CO_3 <\!\!-\!\!> H^+ + HCO_3^- \quad K = 4{,}47 \times 10^{-7} \text{ à } 25°C \quad (K= [HCO_3^-][H^+]/[H_2CO_3]) \quad [4]$$

$$HCO_3^- <\!\!-\!\!> H^+ + CO_3^{2-} \quad K = 4{,}70 \times 10^{-11} \text{ à } 25°C \quad (K= [CO_3^{2-}][H^+]/[HCO_3^-]) \quad [5]$$

From a thermodynamic point of view, the large equilibrium constant associated to equation [3] translates into a weak inherent tendency to produce the acid (K_{eq} = $[CO_2]/[H_2CO_3] \cong 600$) (Chemistry of the Elements (2nd edition, Butterworth Heinemann, p. 310 (1997)).

Equation [3], representing the formation of carbonic acid (H_2CO_3), is in reality the limiting step of the process for producing bicarbonate.

Thus, the use of an enzyme, preferably carbonic anhydrase, which is specific to CO_2 molecules, avoids the step of carbonic acid formation. In other words, the enzyme catalyses the hydration of CO_2 by eliminating the limiting step of the process. As mentioned above, the reaction that allows for the production of bicarbonate in the presence of the enzyme is represented by equation [2]:

$$CO_2 + H_2O \overset{\text{enzyme}}{<\!\!-\!\!>} H^+ + HCO_3^- \quad [2]$$

Reaction [2] allows for the production of an aqueous solution having a high HCO_3^- ion content that is used in the process of producing PPC. This concept is represented in the following equation:

$$HCO_3^- + H^+ + Ca(OH)_2 <\!\!-\!\!> CaCO_3 + 2\, H_2O \quad [6]$$

Equation 6 is the result of the following equations:

$$HCO_3^- <\!\!\longrightarrow H^+ + CO_3^{-2} \quad [1b]$$

$$Ca\,(OH)_2 <\!\!\longrightarrow Ca^{2+} + 2\, OH^- \quad [1c]$$

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$$Ca^{2+} + CO_3^{-2} \longleftrightarrow CaCO_3 \qquad [1d]$$

$$2\,OH^- + 2\,H^+ \longleftrightarrow 2\,H_2O \qquad [1e]$$

From equations [1] and [6], one can see that the reaction for producing PCC performs better in the presence of an enzymatic bioreactor supplied with gaseous CO_2 which in turn directly supplies HCO_3^- to the process for preparing precipitated calcium carbonate. The improvement resides not only in the increased hydration rate of CO_2, but also in the increased amounts of $CaCO_3$ formed in a given reaction time. The variation of Gibbs free energy (ΔG) for each of the reactions will indeed allow one to determine which of the two chemical reactions is favourable from a thermodynamic point of view.

Reaction [6], having a ΔG in the order of -119 kJ/mol, is more favourable from a thermodynamic point of view than reaction [1] which has a ΔG value in the order of -74 kJ/mol. The respective equilibrium constant of these two chemical reactions is calculated using equation [7]:

$$-\Delta G = RT \ln(K_{eq}) \qquad [7]$$

The equilibrium constant of a chemical reaction not containing enzyme is about $9{,}36 \times 10^{12}$ at 298K, while a catalysed reaction making use of an enzyme is about $7{,}24 \times 10^{20}$. While the equilibrium constant is higher for a reaction containing an